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Vacuum Thermal Decompositions of the Nitrate Salts of Hydrazine

Prepared by
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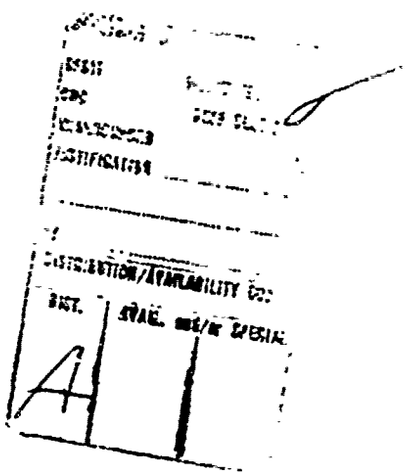

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FOREWORD

This report is published by The Aerospace Corporation, El Segundo, California, under Air Force Contract F04701-71-C-0172. The authors are H. H. Takimoto, P. Breisacher, G. C. Denault, and W. A. Hicks of the Aerodynamics and Propulsion Research Laboratory.

This report, which documents research carried out from March through August 1971, was submitted on 25 January 1972 to Capt Karl J. Hoch, SYAE, for review and approval.

Approved

W. R. Warren, Jr., Director
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Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Karl J. Hoch, Capt, USAF
Project Officer

ABSTRACT

The vacuum thermal decompositions of the combustion intermediates from the reaction of N_2O_4 with N_2H_4 have been investigated. The identity and concentrations of the evolved gaseous products from mononitrate and dinitrate salts of hydrazine as well as ammonium nitrate were determined at successive temperatures until the thermolyses were completed, with a mass spectrometer and differential thermal analyzer.

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I. INTRODUCTION

Hydrazine and alkylated derivatives in combination with N_2O_4 have been used for some time in liquid bipropellant rocket motors. The propulsion systems utilizing these propellants have at times encountered difficulty during rapid start and restart conditions under low-pressure environments where complete combustion of the fuel does not occur. Partially oxidized fuel is accumulated in the combustion chamber wall and nozzle area. As a result, the occurrence of abnormally large ignition overpressures during pulse mode firings have a deleterious effect on engine performance. The expulsion of these combustion intermediates with the exhaust products can also lead to contamination of the spacecraft vehicle surfaces. Previous work has established that the major constituents among the residues from the combustion reactions between N_2O_4 and hydrazine derivatives are the nitrate salts of the fuel [1-3].

Earlier work in our laboratory investigated the thermal decomposition of mononitrate and dinitrate salts of monomethylhydrazine (MMH) [4], which are the residues resulting from the incomplete combustion of N_2O_4 and MMH. Simultaneous mass spectrometric differential thermal analyses of these compounds resulted in the evolution of 11 identifiable species. This study has been extended to include the thermal decomposition of nitrate salts of hydrazine.

II. MATERIALS AND PROCEDURE

The nitrate salts of the fuel were prepared by a careful titration of an ice cold solution of freshly distilled hydrazine with a corresponding equivalent quantity of dilute nitric acid. The water was cautiously removed under reduced pressure, and the mononitrate was purified by repeated dissolution in methanol. Both the mononitrate and dinitrate salts were white crystalline solids having extremely hygroscopic properties. These compounds were stored in a desiccator and used immediately after purification.

Purified $N_2H_4 \cdot HNO_3$ melted at 69-71°C (lit. value 70.7°C) [5], which corresponds to the α-crystalline form. When heated rapidly, while compacted in a capillary tube, the material detonated.

$N_2H_4 \cdot 2HNO_3$ melted at 101-103°C (lit. value 103-104°C) [6] when heated rapidly. A slow rate of heating resulted in bubbling and decomposition starting at approximately 85°C.

The apparatus used in this mass spectrometric differential thermal analyses study was described in our previous report [4]. The system employed a well-regulated temperature-programmed furnace constructed of a silver heating block and a matched pair of thermocouples for recording the temperature. Rapid removal of the decomposed species from the furnace and quick injection into the ion source of the mass spectrometer were achieved by operating under low pressures. Use of a choking orifice with rapid pumping minimized the possibility of solid-gas reactions occurring between the volatile products and the decomposing residue. For all of

the runs, the maximum pressure did not exceed 300μm. By reduction of the dynamic pressure in the flow lines, maximum flow velocities and minimum residence time of the product gases in the sampling system were maintained.

A Bendix time-of-flight mass spectrometer with an inlet system composed entirely of glass and stainless steel was used for the analyses of the evolved species. The pressure in the spectrometer was 2×10^{-7} mm Hg initially, and even during the peak endotherms it did not exceed 1×10^{-6} mm Hg.

The spectrometer enabled the monitoring of continuously entering samples in a recurring cycle on a highly sensitive oscillographic recorder. By the simultaneous imprint of the time and temperature history on the differential thermogram and mass spectral chart, the composition-temperature data profiles of the evolved species were constructed. A small quantity of argon was leaked into the sampling system for referencing all peak intensity data to the inert gas.

In a typical run, 65 mg of the nitrate salt was placed directly into a glass sample holder, together with a Chromel-Alumel thermocouple, and the glass tube was inserted into a cavity of the heating block. The material was outgassed for a suitable period of time, and the mass spectral background was recorded. Heating of the sample was started simultaneously with the recording of the mass spectral readings. A heating rate of 25°C/min and a scanning rate of about 40 sec covering the mass range up to 75 was used. Time data were recorded on the thermogram and the mass

spectral chart. This procedure allowed the correlation of temperature with the mass numbers during the spectral scanning cycle. As in the case of the nitrate salts of MMH, an early appearance of water was noted. This was believed to be caused at least partially by the presence of absorbed water despite precautions during thorough outgassing and transfer of the sample into the vacuum apparatus as quickly as possible. All recorded temperatures were referenced to $0^{\circ}C$.

Figures 1-3 show typical differential thermograms and product profiles obtained during the thermal decomposition. The first endotherm observed for the mononitrate and the dinitrate (Figs. 1 and 2) appeared to be a function of the dryness of the sample, with the drier salts yielding smaller endotherms. Further, the peak endotherms were moved slightly to a higher temperature with larger sample size.

The sensitivity of the mass spectrometer was calibrated for the expected evolved species from the decomposition of the hydrazinium nitrates. Known mixtures of all the gases with the exception of HN_3 were prepared and calibrated independently under flow conditions similar to those of the actual reaction and inlet systems. HN_3 sensitivity was estimated by a cross reference of the values listed for similar compounds in the American Petroleum Institute tables.

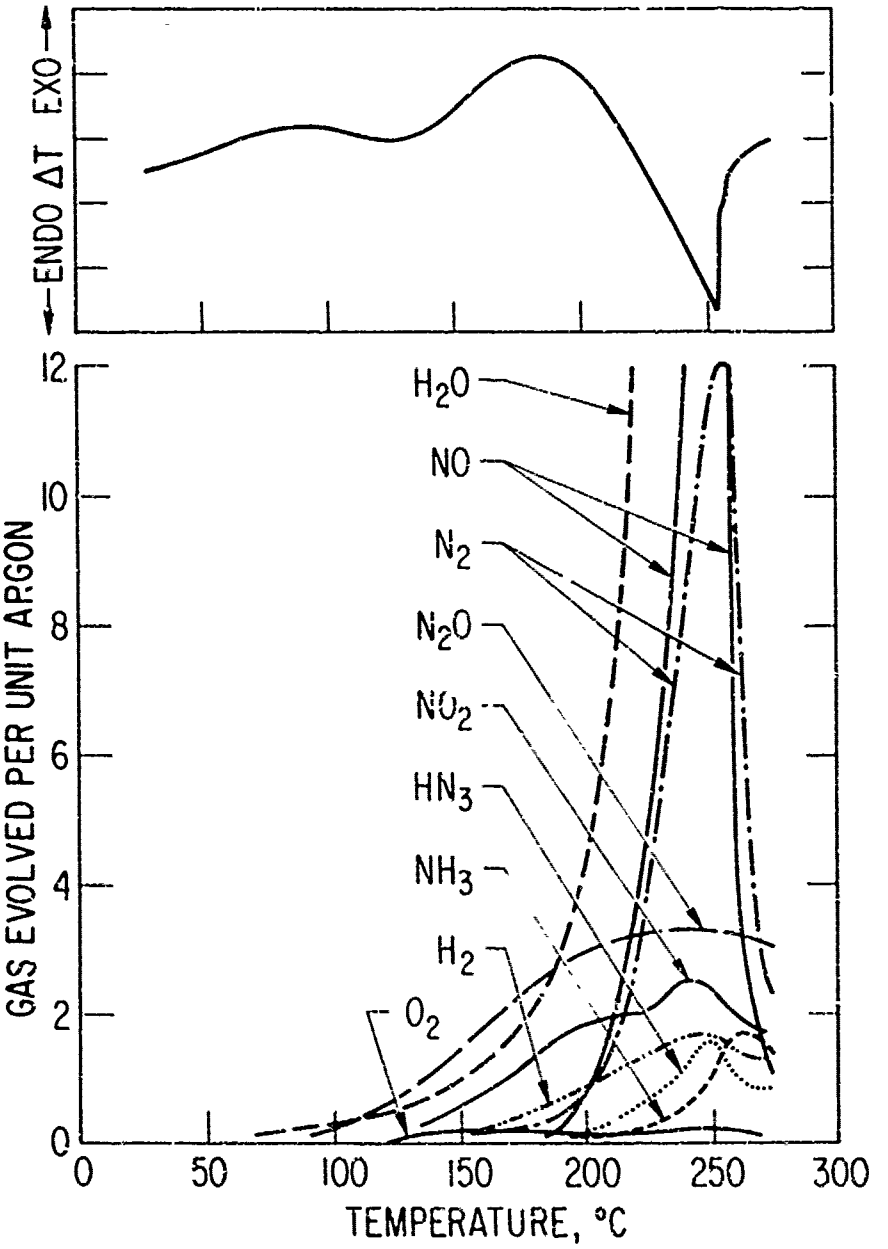

Figure 1. Vacuum differential thermogram and product profile for hydrazinium nitrate

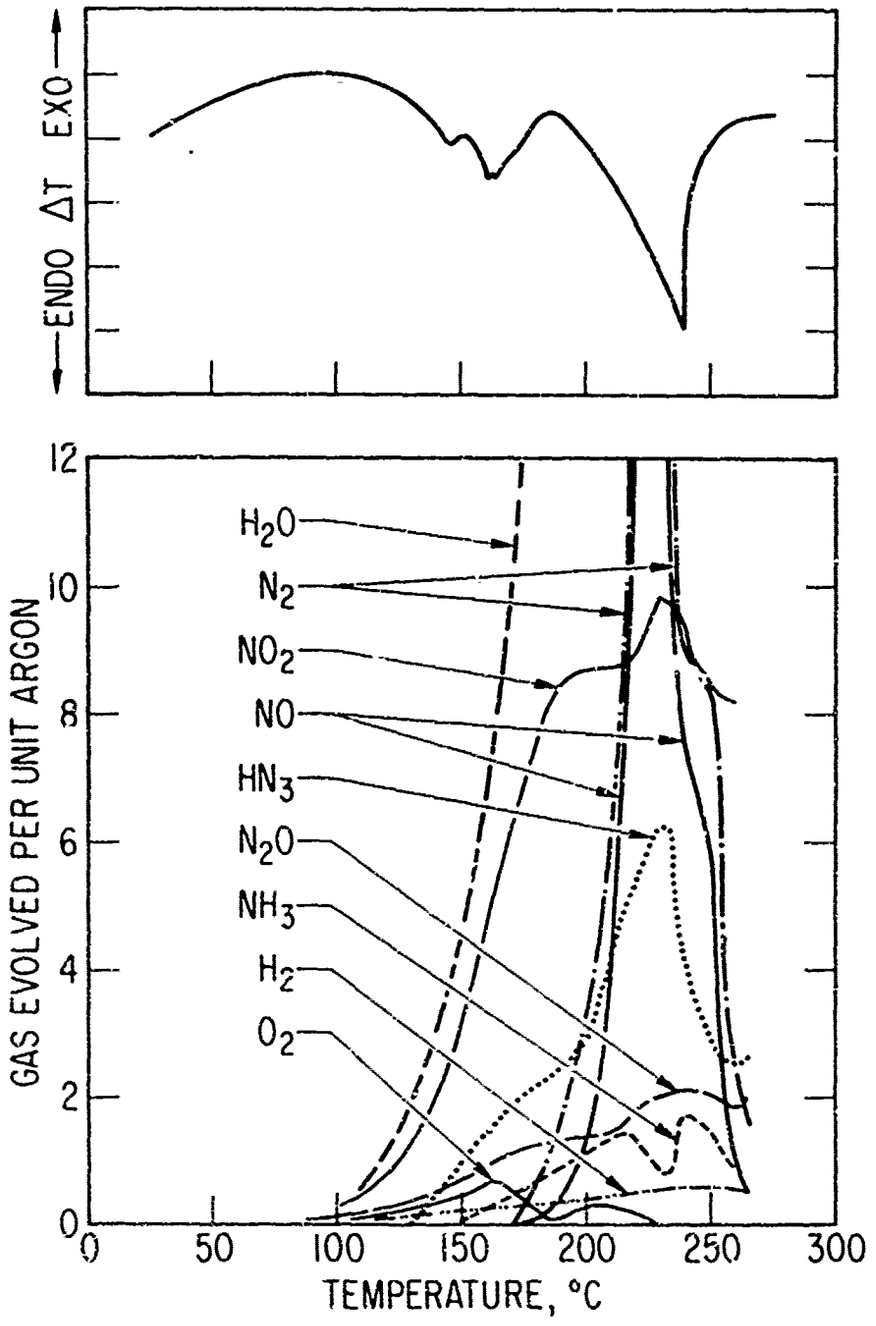

Figure 2. Vacuum differential thermogram and product profile for hydrazinium dinitrate

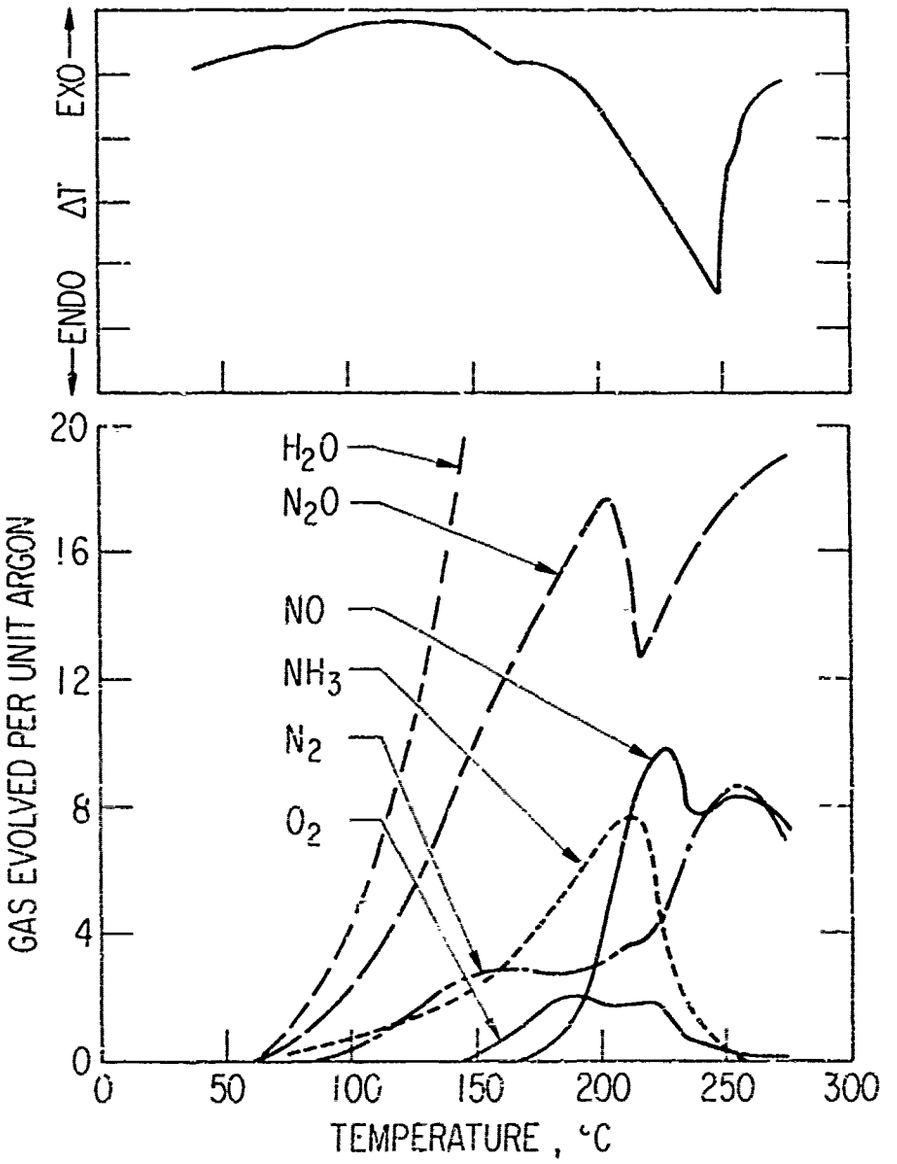

Figure 3. Vacuum differential thermogram and product profile for ammonium nitrate

III. RESULTS AND DISCUSSION

The differential thermograms and the compositions of the evolved gases versus temperature during the thermal decompositions of $N_2H_4 \cdot HNO_3$, $N_2H_4 \cdot 2HNO_3$, and NH_4NO_3 are plotted in Figs. 1-3. Identical temperature scales are used for both graphs. The terminal exotherm in the differential thermograms obtained in the decomposition at ambient pressure was replaced by a large endotherm in vacuum similar to that reported for $MMH \cdot HNO_3$ salts. The observed effect is the net result of the heat released during thermolysis and heat absorbed upon volatilization of the products. Apparently, the heat of vaporization of the substantial amounts of water formed is the dominating factor in determining the shape of the thermogram.

In Fig. 1, it can be seen that the major products evolved were water, NO, and N_2, with evolution starting at approximately 209°C. Consideration of only these major species indicates that the decomposition of $N_2H_4 \cdot HNO_3$ may be described by the following equation, which had previously been proposed by Hodgkinson [7]:

$$4N_2H_4 \cdot HNO_3 \rightarrow 5N_2 + 2NO + 10H_2O$$

Among the minor products found were N_2O, NO_2, NH_3, HN_3, H_2, and O_2. A barely detectable quantity of hydrazine (not shown in Fig. 1) was obtained in some of the runs. This is probably due to the dissociation of the nitrate salt. Further evidence for the occurrence of hydrazinium nitrate dissociation can be seen by a small spectral peak appearing at a mass number of

63, corresponding to HNO_3. Water and N_2O were among the first products evolved at the lower temperatures. The decomposition was complete at about 255 °C.

The results from the vacuum differential thermogram and product profile obtained from the decomposition of $N_2H_4 \cdot 2HNO_3$ are shown in Fig. 2. In comparison to the mononitrate, water was released at lower temperatures (ca 150°C) and was manifested in the first endotherm observed in the thermograms. In addition, a considerable quantity of NO_2 was evolved at these temperatures. In fact, NO_2, which was a minor product in $N_2H_4 \cdot HNO_3$ decomposition, became one of the major species, together with water, NO, and N_2. A substantially greater amount of HN_3 was also produced, whereas the remaining expected species, N_2O, NH_3, H_2, and O_2, were found as minor products. Again, with the observed major products, the decomposition reaction for $N_2H_4 \cdot 2HNO_3$ may be written as:

$$N_2H_4 \cdot 2HNO_3 - N_2 + NO + NO_2 + 3H_2O$$

However, the decomposition reaction of the double nitrate salt is very complex, and the minor products can play an important role in determining the relative quantity of the major species. Thus, no single equation can be written to represent accurately the species produced.

Among the evolved species from the thermolyses of nitrate salts of hydrazine, a gaseous product having a mass number of 43 was observed and attributed to hydrazoic acid (HN_3). This product is an extremely shock- and heat-sensitive energetic compound that may be formed by

the nitrosation of the hydrazine followed by rearrangement and dehydration. The presence of this explosive compound is consistent with the identification of methylazide discovered in our previous work during the thermolysis of $MMH \cdot HNO_3$. These results are also analogous to the results obtained by Dauerman, et al. [8] where HN_3 was observed when N_2O_4 condensed on N_2H_4 at a low temperature was allowed to warm up slowly. These results are of particular interest in that HN_3 would also be formed during the operation of N_2O_4/hydrazine bipropellant motors under high-altitude conditions. Although this azide would not be accumulated under a low-pressure environment, it nevertheless is capable of triggering the detonation of the nitrate salts accumulated in the combustion chamber walls. Thus, if sufficient quantity of the combustion intermediate had been formed from previous firings, the resultant effect would be an abnormally high ignition overpressure. Such pressure spiking phenomenon had been observed in the operation of bipropellant motors under a low-pressure environment.

The decomposition of ammonium nitrate [9] has been described as follows:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

The reaction, however, is much more complicated, as evidenced by the results shown in Fig. 3. In addition to water and N_2O, smaller amounts of NO, NH_3, and N_2 were also obtained. The formation of the latter two species during the decomposition of ammonium nitrate has previously been reported [9]. A small peak at mass number of 63 (HNO_3) was also observed. No evidence for the presence of NO_2 was found, although a small quantity

may have been present but was undetected since the mass spectra is obscured by interfering compounds.

This study of the combustion intermediates from the reaction of N_2O_4 with hydrazine has defined the temperature range required for the removal of these hydrazine nitrates by thermal degradation. The identity of the evolved species and their respective concentrations as a function of increasing temperature have also been obtained.

REFERENCES

1. Christos, T.; Miron, Y.; James, H.; and Perlee, H.; J. Spacecraft Rockets, 4 (9), 1224 (1967).
2. Perlee, H.; Christos, T.; Miron, Y.; and James, H.; J. Spacecraft Rockets, 5 (2), 233 (1968).
3. Mayer, S. W.; Taylor, D.; and Schieler, L.; Combust. Sci. and Technol., 1, 119 (1969).
4. Breisacher, P.; Takimoto, H. H.; Denault, G. C.; and Hicks, W. A.; Combustion and Flame, 14, 397 (1970).
5. Sommer, F., Z. Anorg. Chem., 86, 71 (1914).
6. Sabanejeff, A., Z. Anorg. Chem., 20, 21 (1899).
7. Hodgkinson, W. R. E., J. Soc. Chem. Ind., 32, 519 (1913).
8. Ray, A. B.; Koehler, G.; Selzer, G. E.; and Dauerman, L.; AIAA, 6, 2186 (1968).
9. Rosser, W. A.; Inami, S. H.; and Wise, H.; J. Phys. Chem., 67, 1753 (1963).